The Rate of Reaction of Nitric Oxide and Oxygen

DISSERTATION

SUBMITTED TO THE BOARD OF UNIVERSITY STUDIES OF
THE JOHNS HOPKINS UNIVERSITY IN CONFORMITY
WITH THE REQUIREMENTS FOR THE DEGREE
OF DOCTOR OF PHILOSOPHY

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BY
RUDOLPH LEONARD HASCHE
BALTIMORE

June 1924

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ACKNOWLEDGMENT

The author wishes to express his deepest gratitude to Professor Walter A. Patrick at whose suggestion and under whose direction this investigation was carried out. He also wishes to express his thanks to Professors J. C. W. Frazer and E. E. Reid and to Dr. Wm. M. Thornton, Jr., for valuable advice and inspiration received in the laboratory and in the lecture room.

STUDIES ON THE RATE OF OXIDATION OF NITRIC OXIDE
I. A NEW METHOD OF MEASURING THE VELOCITY OF A RAPID GASEOUS REACTION

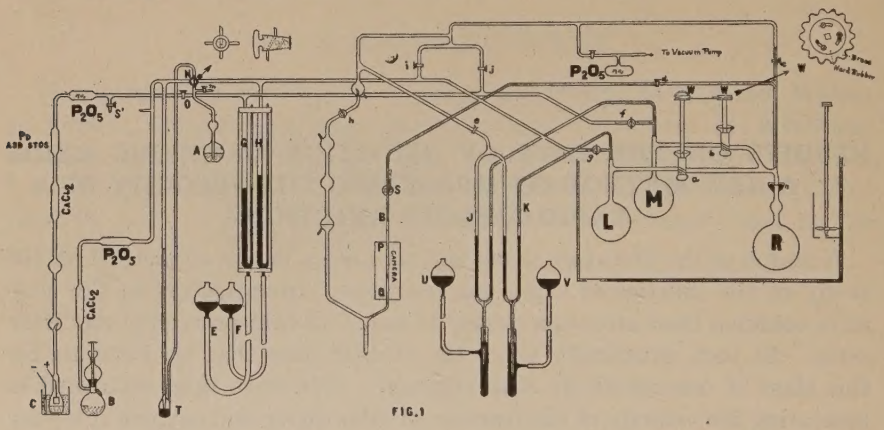
A search of the literature shows the need of an improved method for the study of the kinetics of rapid gas reactions. Investigators in this field have confined their attention largely to reactions that proceed at moderate rates. In fact, practically all of the reliable data that we have are for this class of comparatively slow reactions. We have been interested in measuring the velocity of the reaction of nitric oxide and oxygen; it is very rapid, especially at the lower temperatures, 0–30°, since it possesses a marked negative temperature coefficient. Bodenstein[1] developed an apparatus for the study of this reaction, following its course by direct reading of the pressure changes as indicated by an α-bromonaphthalene manometer. He realized that his results at 0° were subject to considerable error. It is very desirable to study the reaction at short time intervals in the beginning when it is progressing very rapidly. This was not possible in Bodenstein's work due to (1) the uncertainty of zero time and (2) his inability to make direct readings of the rapidly moving manometer meniscus. In many cases, the reaction had proceeded 20–30% to completion before the first reliable reading was taken. A careful study of the reaction in the first few seconds should help us to settle the question as to the occurrence of autocatalysis.

[1] Bodenstein, *Z. Elektrochem.*, **24**, 183 (1918).

It occurred to us that an apparatus could be devised to record the pressure changes (as indicated by a liquid manometer) on a photographic film at much shorter time intervals than would be possible by direct reading of the manometer. After much experimenting, the apparatus was developed which is described in this article; the results given in the second article indicate the possibilities of the apparatus and technique in the study of rapid gaseous reactions accompanied by a change in the number of molecules. The apparatus is somewhat similar to that employed by Bodenstein,[1] being modified so as to allow of a rapid flow of the reacting gases into the reaction chamber.

Apparatus

The experimental method used was the manometric-volumetric; the volume was kept constant and the pressure change followed by photographing an α-bromonaphthalene manometer. The apparatus, exclusive of the timing mechanism and camera, is shown in Fig. 1.



The oxygen was generated electrolytically in the cell (C) with platinum electrodes and dil. sulfuric acid as the electrolyte. The gas passed over freshly prepared palladium asbestos to remove traces of hydrogen and was dried by phosphorus pentoxide. It was delivered at Stopcock O. Previous to using the oxygen for an experiment, it was generated for several days and liberated through Stopcock S. The generator worked on the Kipp principle, automatically cutting off the current when the pressure in the anode compartment became slightly more than atmospheric.

The nitric oxide was generated slowly and continuously in (B) from the interaction of mercury on lead chamber crystals dissolved in sulfuric acid. The nitrosyl sulfuric acid was made by passing sulfur dioxide gas through fuming nitric acid cooled by ice water. The crystals were filtered by suction through an alundum crucible, washed with a little glacial acetic acid

and then freely with carbon tetrachloride. They were dried in a vacuum desiccator over sulfuric acid. The nitric oxide generator was first evacuated through Stopcock N; then by turning the ground glass stopper of the generator, mercury could be introduced into the nitrosyl sulfuric acid solution. A few drops of mercury added every few days insured the continuous flow of a stream of nitric oxide. The gas was dried over calcium chloride and phosphorus pentoxide. When nitric oxide was not being used, the 4-way Stopcock N was closed to the rest of the apparatus and the nitric oxide bubbled through the mercury trap (T) and out through the sulfuric acid bottle at (A). The latter served as a trap allowing an exit for excess of nitric oxide and preventing entrance of air. The mercury trap (T) protected (A) during evacuation.

The purity of the nitric oxide was tested by drawing off samples at the 3-way Stopcock M. The gas was analyzed by the method of Moser,[2] using a strong solution of potassium permanganate acidified with sulfuric acid as the oxidizing and absorbing liquid. The residual gaseous impurities amounted to less than 0.5%.

The leveling burets (G) and (H) were used to regulate the pressure of oxygen and nitric oxide in their respective storage bulbs (M) and (L). The burets could be evacuated through Stopcocks j and i and were connected to the storage bulbs through Stopcocks f and g.

The nitric oxide and oxygen storage bulbs (L) and (M) and the reaction chamber (R) were immersed in a thermostat kept constant to $\pm 0.01°$. The water line extended up to the mercury seals of the large Stopcocks a and b; the glass tubing above the water line was all capillary. Gas pressures in the storage bulbs were read by a cathetometer from the Y-shaped manometers (J) and (K). The right limb of each manometer was capillary over a part of its length as shown in the figure; the left limbs were open to the vacuum through Stopcock e. When a pressure reading was made on either manometer, the mercury in the right limb was always brought to the same mark just below the capillary by means of the leveling bulbs (U) and (V). Thus a constant, known volume was always maintained. The storage bulbs could be evacuated either through Stopcocks f, g, i and j or through a, b and c. The bulbs were connected directly to the reaction chamber (R) by specially designed mercury-sealed vacuum stopcocks of 6 mm. bore; the ends of the keys were square to accommodate brass sprocket wheels, the design of which is shown in detail at (W). The sprockets were adjustable to one-half the width of a tooth and were connected by a brass ladder chain. The whole mechanism made it possible to open and close the two stopcocks synchronously, and the tubing of 6 mm. bore permitted a very rapid flow of the gases into the reaction chamber.

The large and small surface reaction chambers could be connected with

[2] Moser, *Z. anorg. Chem.*, **121**, 313 (1922).

the apparatus by the mercury-sealed normal grindings at (n). They were of approximately the same capacity, the large surface vessel being filled with very fine glass wool. Pressure in the reaction chamber was followed by the α-bromonaphthalene manometer (B) through Stopcock d. The recording part of the manometer on the right limb was thin-walled, 3 mm. tubing calibrated in millimeters on a dividing engine. Every tenth division was omitted so as to aid in reading the scale from the film. The camera is not shown in Fig. 1; it was a light-tight box enclosing the manometer between (P) and (Q). The difference in height of the left limb of the manometer was negligible because of the large volume of α-bromonaphthalene in the bulb. The other bulbs could be used for work at higher pressures and also served as very effective traps, in case the pressure on the right side of the manometer was excessive due to accidental opening of Stopcock d to atmospheric pressure while Stopcock h was closed. Since the coefficient of expansion of α-bromonaphthalene is very large (0.0015 per degree), its temperature at the time the measurements were made must be known. Its temperature was read on the thermometer (S) dipping into a plaster of paris well, filled with mercury.

The oxygen storage bulb was calibrated by mercury before sealing into the apparatus. The nitric oxide bulb and two reaction chambers were calibrated from the oxygen bulb by expansion of gas from the latter into the others, and the pressure changes recorded by the mercury manometers gave all the data required to calculate the unknown volumes by making use of the gas laws. The α-bromonaphthalene served as check on the mercury manometers.

The timing mechanism and camera are shown in Fig. 2. Exposures of the manometer were made on a circuit film which was mounted on the drum of a kymograph. The kymograph was enclosed in a box, light-tight with the exception of a narrow slit formed by two wooden strips holding the manometer. The shutter (S) was an aluminum tube open at the opposite ends of the diameter. This was free to rotate on shafts fitting into bearings at either end. At the top of the shutter, a clock-spring movement produced a spinning tension on the cylinder when the escapement (R) was released by a current through the electromagnet (e). The double-dog escapement lever allowed the cylindrical shutter to rotate through only an angle of 180° for each impulse through the electromagnet. By this arrangement the wide aperture of a focal plane shutter was obtained. The time of exposure was about $^1/_{25}$ of a second.

An Eastman timer served as the movement for the interval timer. Around the dial of the clock was a Bakelite plate turned on a lathe to the form shown in the diagram in Fig. 2. Thirty holes 2.5 mm. in diameter were drilled for a distance into the inner rim of the plate; opposite these on the outer, raised rim thirty holes 5 mm. in diameter were drilled to the

same depth as the first set. Each pair of holes was connected by a third drilled at right angles and the outer opening closed with a set screw. In the diagram of (T) in Fig. 2, a cross section through a mercury well shows the construction.

Electrical connection was made through the induction coil (C), actuating the camera shutter, when the hand of the clock (itself connected to one pole of the battery) passed through a mercury drop on the inner rim of the timer plate. The current flowed through the mercury trough to the resistance box type plug which dipped into the mercury. The plug made connection with the brass ring (B) which was connected to the other pole of the battery. By inserting plugs at the time intervals desired, exposures were made automatically on the rotating film. The plugs were drilled at the ends and piano wire contacts driven into them. The piano wire insured good contact and prevented amalgamation of the brass. The other contact with the mercury was made by the platinum tip soldered to the second hand of the clock. The amount of mercury in the wells could be so regulated that the tip of the second hand passed through the globule only when a plug had been inserted, thus raising the level of the mercury by a very small amount. Three cells of an Edison storage battery worked the timer circuit, and the electromagnet operated on the 110-volt d. c. line through the lamp bank (L).

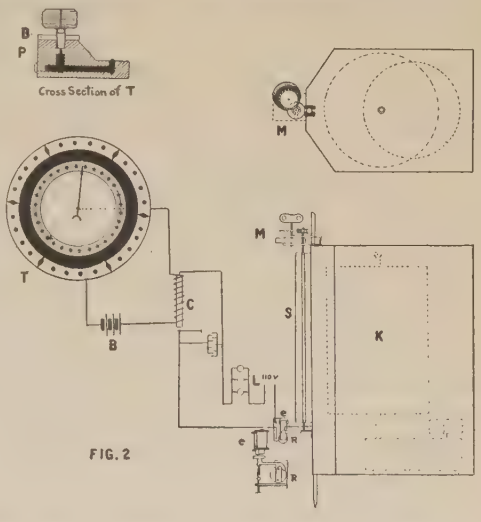


FIG. 2

An arc lamp operating on the 110-volt d. c. line and using 5 amperes furnished the illumination for the α-bromonaphthalene manometer. A mirror reflected a narrow beam of light of even intensity on the shutter.

Method of Measurement

The apparatus exclusive of the gas generating systems was evacuated to 0.003 mm. preliminary to making a run. Great care was necessary to evacuate both sides of the manometers at the same rate, otherwise the manometer liquid might be thrown into the storage bulbs or reaction chamber. After evacuation, all stopcocks except (f) and (g) were closed. Oxygen was admitted to the storage bulb by carefully opening Stopcock O. When approximately the desired pressure was obtained, Stopcock O was

closed and a finer adjustment was made by raising or lowering the leveling bulb (E). Stockcock f was then closed, and after bringing the mercury to the calibration mark on the right limb by means of the leveling bulb, the pressure was read by the cathetometer. The same procedure was followed with the nitric oxide, admitting it through the 4-way Stopcock N. After the pressures of the oxygen and nitric oxide had been read and recorded, the zero of the α-bromonaphthalene manometer was read and also a reference mark which was etched on the graduated manometer scale within the range of pressure change as recorded on the film. The temperature of the α-bromonaphthalene was also read.

The room was darkened and the film 20 cm. in width mounted on the kymograph, the end of the film being fastened with adhesive tape. The kymograph was placed in the camera box with the drum at the proper focal distance from the manometer. It was started rotating by throwing the release lever, the camera closed and the arc lamp and clock started. At one second before zero time, the mechanism for the turning of Stopcocks a and b was set in motion. It required about three seconds for the whole operation of opening and closing, although the actual period during which the keys were open to the reaction chamber was never more than one second. No back diffusion occurred in any of the experiments and in the majority of the cases equilibrium was attained. No attention to the apparatus was required during a run unless the time intervals were lengthened, when plugs were removed from the timer. Exposures on the film could be made as close together as 3 mm. which gave a continuous picture of the manometer with no intervening spaces. The length of the runs varied from four minutes to fifteen, depending on the frequency of exposures and the temperature at which we were working.

When the run was completed, the film was developed immediately and the pressures of the residual gases in the storage chambers read on the mercury manometers. The difference between the initial and final readings gave a means of calculation of the initial pressures of oxygen and nitric oxide, since the volumes of the storage bulbs and reaction chamber were known. The system was immediately evacuated.

Several possible sources of error which we have considered as negligible should be mentioned. In the first place, we have assumed that there is no change of volume of the reaction chamber due to the manometer. This assumption is justifiable since the maximum change in volume due to the manometer was about 0.9 cc. which is less than the experimental error in the calibration of the reaction chamber by the gaseous expansion method. We have assumed that the heat of the reaction was not sufficient to affect the temperature of the reaction mixture and hence alter the observed velocity. This was verified by sealing a thermometer into a reaction chamber and introducing the reacting gases under actual experimental condi-

tions. The maximum rise in temperature occurred in the first minute and was only 0.3°, which is negligible. Finally, the α-bromonaphthalene manometer was almost instantaneous in its response to pressure changes within the system. None of the photographs obtained in the investigation given in the second paper shows any evidence of a lag.

Summary

An apparatus has been described which is capable of measuring accurately the velocity of a rapid gaseous reaction.

II. THE VELOCITY OF THE REACTION BETWEEN NITRIC OXIDE AND OXYGEN AT 0° AND 30°

A number of investigators have studied the kinetics of the reaction between nitric oxide and oxygen. It was the subject of a long controversy between Raschig and Lunge. They used similar experimental methods, absorbing the reacting gaseous mixture in sodium hydroxide or sulfuric acid and titrating the amount of nitrogen dioxide formed with potassium permanganate. Raschig claimed experimental evidence pointing to the formation of nitrogen trioxide as an intermediate product; while Lunge's results indicated that nitrogen dioxide was formed directly, strictly in accordance with the law of a third-order reaction. Raschig's view regarding the intermediate, nitrogen trioxide, is also held by Briner and co-workers,[1] and by Jolibois and Sanfourche.[2] That the reaction possesses a small, but marked, negative temperature coefficient was first noted by Foerster and Blich.[3] Recently, Briner, Pfeiffer and Malet[4] have studied the reaction at low temperatures, down to —193°; Bodenstein,[5] in 1918, worked at the temperatures 0°, 30°, 60° and 90°; later, Bodenstein and Linder[6] con-

[1] Briner and Fridori, *J. chim. phys.*, **16**, 279 (1918). Briner and Fridori, *Helvetica Chim. Acta*, **16**, 181 (1918). Briner, Niewiazski and Wiswald, *J. chim. phys.*, **19**, 290 (1921).

[2] Jolibois and Sanfourche, *Compt. rend.*, **168**, 235 (1919). Sanfourche, Bl. **25**, 533, 646 (1919).

[3] Foerster and Blich, *Z. angew. Chem.*, **23**, 2017 (1910).

[4] Briner, Pfeiffer and Malet, *J. chim. phys.*, **28**, 25 (1924).

[5] Bodenstein, *Z. Elektrochem.*, **24**, 183 (1918).

[6] Bodenstein and Linder, *Z. physik. Chem.*, **100**, 87 (1922).

tinued the velocity measurements at still higher temperatures, up to 394°. The results confirm those of Lunge that the reaction is one of the third order. Furthermore, Bodenstein states that the reaction occurs entirely in the gas volume, in other words, is a homogeneous gaseous reaction uncatalyzed by the walls of the reaction vessel. If this were true, it would be an exceptional case. It seemed more questionable in the light of recent research, as day by day the number of reactions that are uncatalyzed by the surface of the reaction vessel is being narrowed down. In order to answer this question, the present work was undertaken. The surface-to-volume ratio was increased approximately 140 times by filling the reaction chamber with glass wool.

The apparatus and experimental procedure described in the preceding paper was employed. With partial pressures of nitric oxide and oxygen of approximately 20 mm. of mercury, the reaction proceeded at a rate that could be measured very satisfactorily.

Method of Calculation

An excess of oxygen was used in all of the experiments. Calculations of the velocity constants, therefore, are based on the decrease in pressure in terms of nitric oxide with time expressed in seconds. In order to make the calculations of the velocity constants for the different experiments comparable, all readings of the α-bromonaphthalene manometer were corrected to 15°. The temperature coefficient of expansion and density of the manometer liquid were determined under actual experimental conditions. The mercury and α-bromonaphthalene manometers were opened to the same pressure and read at two different temperatures. Correction for the association of nitrogen dioxide into the tetra-oxide was applied to the observed pressure decrease expressed in millimeters of α-bromonaphthalene corrected to 15°. The speed of this reaction is so great that it may be neglected, and the degree of dissociation calculated from the equilibrium constant. Bodenstein and Linder[7] made a careful study of the equilibrium and give an empirical formula which expresses the relation between their observed value of K_p and the absolute temperature, pressure being expressed in atmospheres: $\text{Log } K_p = (2692/T) + 1.751 \log T + 0.0048\ T - 7.144 \times 10^{-6} + 3.0622$. Calculation according to this formula gives a value for K_p of 0.0178 at 0° and 0.2105 at 30°.

The degree of dissociation of nitrogen tetra-oxide, designated by α, may be calculated according to the equation, $\alpha = \sqrt{\frac{K_p}{4P + K_p}}$, where P denotes the pressure due to the equilibrium, $N_2O_4 \rightleftharpoons 2NO_2$, and is expressed in atmospheres. Different values of P (converted over into millimeters of α-bromonaphthalene at 15°) were substituted in Equation 1 and the values

[7] Ref. 6, pp. 37–105.

of α thus obtained furnished the necessary data for the construction of the curves shown in Fig. 1. The curves give the relation between the observed decrease in pressure, denoted by Δp, and the degree of dissociation of nitrogen tetra-oxide. The decrease in pressure, which is represented by the equation, $2NO + O_2 = 2NO_2$, we have designated by x and it is expressed in mm. of α-bromonaphthalene at 15°. It is obtained by substitution in the expression $x = \Delta p/(\alpha - 2)$.

The method for the calculation of the velocity constants differed from that employed by other investigators. The constants found in the paper are "instantaneous" velocity constants. The decrease in pressure of nitric oxide expressed in millimeters of α-bromonaphthalene was plotted on a

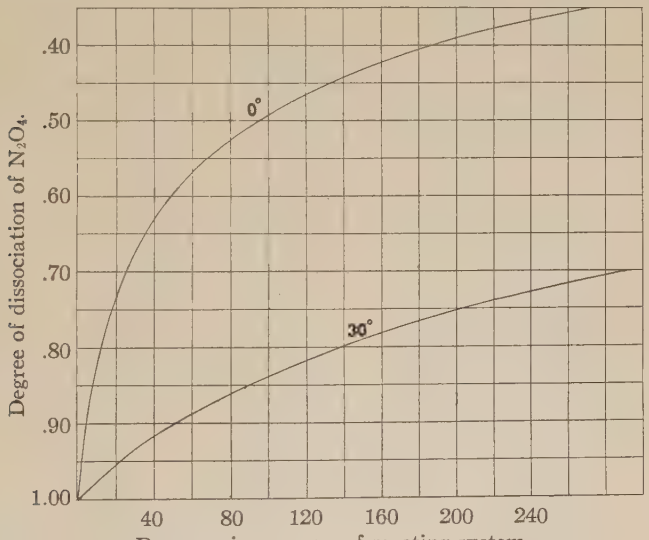


Fig. 1.—Mm. of α-bromonaphthalene at 15°.

large scale against time in seconds; the slope of the curve at any point was read directly by the mirror method developed in this Laboratory by Latshaw.[8] This method seems far superior to the evaluation of velocity constants by the use of the integrated expression; it certainly leads to truer values than are obtained by taking the mean slope between two pressure readings, and is much easier to use than an interpellation formula. It is very essential that the curves be drawn accurately for the successful use of the mirror method. The velocity constants were obtained by substitution in the equation for a reaction of the third order, $k = (dp/dt/[NO]^2[O_2]$.

In the tables that follow, a and b represent measured initial pressures of oxygen and nitric oxide, respectively, both expressed in millimeters of α-bromonaphthalene. In the column marked Δp is found the decrease in

[8] Latshaw, *J. Am. Chem. Soc.*, **47**, 793 (1925).

pressure as read from the film, corrected to 15°. The image of the meniscus on the film was very sharp and could be read by the aid of a vernier scale and reading glass with an accuracy of ±0.1 mm. This is well within the accuracy of the mercury manometer readings which was ±0.05 mm. The column designated α gives the degree of dissociation of nitrogen tetroxide corresponding to each pressure reading.

TABLE I

RESULTS

EXPERIMENT 2

Small surface at 30°. $a = 145.7$; $b = 210.0$

$T°$	Δp	α	x	dp/dt	$k \times 10^{-7}$	$T°$	Δp	α	x	dp/dt	$k \times 10^{-7}$
6	8.0	0.980	7.9	2.350	4.52	138	71.9	0.869	63.5	0.304	5.37
12	15.2	.963	14.7	2.050	4.80	144	72.8	.868	64.3	.294	5.38
18	21.1	.950	20.0	1.846	5.08	150	73.9	.866	65.1	.276	5.38
24	26.3	.939	24.8	1.650	5.30	160	75.5	.865	66.7	.252	5.44
30	31.4	.931	29.4	1.433	5.39	170	77.1	.863	67.8	.236	5.47
36	35.8	.923	33.2	1.250	5.39	180	78.5	.861	68.9	.219	5.44
42	39.1	.918	36.1	1.107	5.32	190	79.9	.859	70.0	.204	5.50
48	43.3	.911	39.8	0.970	5.39	200	81.2	.858	71.1	.186	5.43
54	46.5	.906	42.5	.857	5.31	210	82.4	.857	72.1	.172	5.40
60	49.4	.901	45.0	.795	5.48	220	83.3	.856	72 8	.168	5.56
66	52.1	.898	47.3	.690	5.27	230	84.2	.854	73.5	.154	5.38
72	54.3	.895	49.1	.643	5.32	240	85.4	.853	74.5	.144	5.43
78	56.4	.891	50.9	.590	5.32	250	86.2	.851	75.1	.140	5.55
84	58.5	.889	52.7	.543	5.33	260	87.1	.850	75.7	.132	5.49
90	60.4	.886	54.2	.510	5.40	270	87.9	.849	76.3	.123	5.34
96	62.3	.883	55.8	.464	5.33	280	88.6	.848	76.9	.116	5.46
102	63.9	.880	57.0	.443	5.42	300	90.1	.847	78.2	.106	5.47
108	65.2	.879	58.2	.420	5.48	320	91.4	.846	79.1	.096	5.37
114	66.6	.877	59.3	.384	5.32	370	94.3	.842	81.4	.078	5.44
120	68.2	.875	60.6	.362	5.39	420	96.8	.840	83.4	.062	5.39
126	69.5	.873	61.7	.340	5.40	470	98.8	.838	85.0	.053	5.46
132	70.8	.871	62.7	.324	5.46					Av.	5.40

EXPERIMENT 4

Large surface at 30°. $a = 146.4$; $b = 200.5$

6	7.8	0.979	7.7	4.300	9.05	144	70.2	0.872	62.3	0.295	6.09
12	14.2	.964	13.7	2.025	5.09	150	71.3	.871	63.1	.280	6.09
18	19.7	.952	18.9	1.625	4.96	160	73.4	.869	64.9	.254	6.24
24	24.9	.943	23.6	1.483	5.14	170	74.7	.866	65.9	.243	6.40
30	29.7	.933	27.9	1.283	5.17	180	76.1	.864	67.0	.234	6.66
36	33.9	.928	31.6	1.117	5.16	190	77.5	.863	68.1	.224	6.92
42	37.4	.921	34.7	1.023	5.33	200	78.8	.861	69.2	.210	7.05
48	40.6	.915	37.5	0.900	5.25	210	80.2	.859	70.3	.194	7.10
54	43.8	.910	40.2	.800	5.20	220	81.3	.858	71.2	.185	7.25
60	46.6	.906	42.6	.724	5.25	230	82.4	.857	72.1	.172	7.30
66	49.0	.902	44.6	.675	5.36	240	83.4	.856	72.9	.161	7.32
72	51.4	.899	46.6	.638	5.33	250	84.3	.855	73.7	.151	7.37
78	53.6	.896	48.6	.590	5.63	260	85.3	.853	74.4	.144	7.48
84	55.6	.893	50.3	.548	5.71	270	86.2	.852	75.1	.138	7.65
90	57.5	.891	51.9	.504	5.70	280	87.1	.851	75.8	.130	7.70
96	59.3	.888	53.3	.468	5.70	300	88.6	.849	77.0	.124	8.26
102	60.8	.885	54.5	.440	5.72	320	90.0	.847	78.1	.118	8.80
108	62.4	.883	55.8	.412	5.76	370	93.3	.844	80.8	.092	9.24
114	63.9	.880	57.1	.388	5.82	420	95.9	.842	82.8	.076	9.81
120	65.3	.878	58.2	.364	5.84	470	98.4	.840	84.8	.062	10.54
126	66.7	.877	59.4	.351	5.99	520	100.3	.837	86.2	.052	10.93
132	67.9	.875	60.4	.330	6.04						
138	69.1	.873	61.3	.316	6.12						

TABLE I (*Concluded*)

EXPERIMENT 6

Large surface at 0°. $a = 127.5$; $b = 168.7$

$T°$	Δp	a	x	dp/dt	$k \times 10^{-7}$	$T°$	Δp	a	x	dp/dt	$k \times 10^{-7}$
8	15.1	0.773	12.3	2.050	8.90	88	69.0	.547	47.5	0.436	10.03
12	20.5	.734	16.2	1.875	9.07	92	70.3	.544	48.3	.410	9.96
16	25.8	.698	19.8	1.625	9.05	96	71.5	.542	49.0	.390	9.94
20	29.4	.678	22.2	1.483	9.11	100	72.7	.540	49.8	.368	9.92
24	33.0	.661	24.6	1.327	9.03	104	73.8	.538	50.5	.348	9.89
28	36.7	.642	27.1	1.184	8.99	108	75.0	.535	51.2	.330	9.84
32	40.0	.630	29.2	1.083	9.04	112	76.0	.532	51.8	.320	9.98
36	43.1	.619	31.2	0.983	9.06	116	77.0	.530	52.4	.310	10.11
40	46.3	.607	33.2	.887	8.98	120	78.0	.529	53.0	.300	10.27
44	48.8	.598	34.8	.833	9.15	124	79.0	.527	53.6	.286	10.24
48	51.2	.592	36.3	.790	9.38	128	79.9	.525	54.1	.281	10.44
52	53.5	.585	37.8	.740	9.52	132	80.8	.523	54.7	.270	10.55
56	55.8	.578	39.2	.707	9.82	136	81.6	.522	55.2	.258	10.50
60	57.8	.573	40.5	.648	9.68	140	82.4	.521	55.7	.252	10.69
64	59.7	.568	41.7	.600	9.61	148	83.8	.518	56.6	.226	10.35
68	61.4	.564	42.8	.570	9.77	160	86.0	.514	57.9	.201	10.37
72	63.2	.560	43.9	.530	9.69	180	89.1	.509	59.8	.176	10.78
76	64.7	.556	44.8	.502	9.71	200	92.0	.504	61.5	.152	11.03
80	66.1	.553	45.7	.472	9.88	220	94.3	.500	62.9	.128	10.77
84	67.6	.550	46.8	.450	9.99	240	96.4	.497	64.3	..	...

EXPERIMENT 9

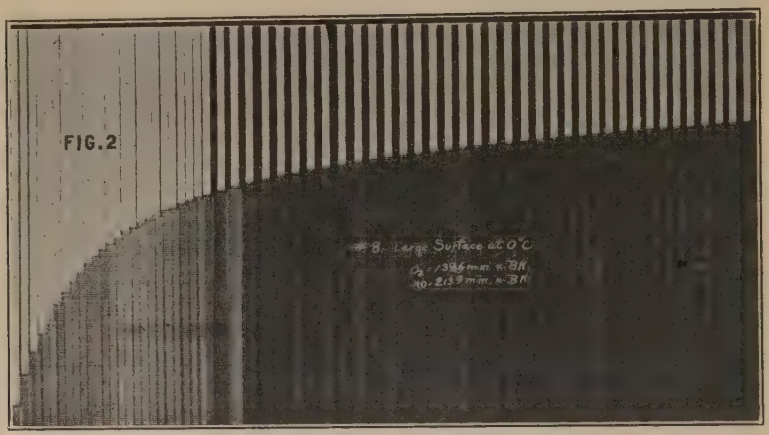
Small surface at 0°. $a = 232.4$; $b = 215.6$

12	44.9	0.611	32.3	3.600	9.89	114	134.5	0.447	86.6	0.340	12.97
18	60.6	.566	42.3	3.170	9.72	120	136.1	.446	87.6	.318	13.45
24	72.4	.540	49.6	2.280	9.20	126	137.6	.444	88.4	.290	13.38
30	83.1	.519	56.1	1.900	10.08	132	138.9	.443	89.2	.270	13.63
36	90.5	.506	60.6	1.417	9.47	138	140.0	.442	89.9	.256	14.02
42	97.5	.495	64.7	1.217	9.76	144	141.2	.441	90.6	.232	13.82
48	103.1	.487	68.2	1.109	10.74	150	142.3	.440	91.3	.208	13.53
54	107.7	.480	70.9	0.933	10.44	160	143.7	.438	92.0	.197	13.84
60	112.2	.474	73.5	.833	11.15	170	145.8	.436	93.2	.176	14.84
66	115.9	.469	75.7	.706	10.93	210	150.6	.431	96.0	.124	16.07
72	119.0	.465	77.5	.620	10.90	250	154.4	.427	98.7	.096	18.19
78	121.9	.462	79.1	.551	10.90	310	157.8	.424	100.1	.064	20.39
84	124.4	.459	80.7	.490	11.00	360	161.0	.421	101.9	.056	26.19
90	126.8	.456	82.1	.450	11.24	410	163.0	.419	103.1	.040	35.01
96	129.0	.454	83.5	.420	11.93	460	164.6	.418	104.1	.028	39.86
102	130.9	.452	84.6	.402	12.63	510	165.7	.417	104.7	..	...
108	132.8	.449	85.6	.380	13.13						

Discussion of Results

We have included in the tables only one experiment showing the results obtained under a given set of conditions. Duplicate runs were made and excellent checks obtained in every instance. Expt. 2 shows that the equation for a third-order reaction is obeyed rigidly. Another experiment, not included, gives an average for the constants of 5.46 which compares well with 5.40, the average of Expt. 2. In Expt. 4, where the reaction chamber was filled with glass wool, the increasing velocity constants toward the end of the reaction indicate that the order of the reaction has been reduced; in other words, the mechanism has been changed. A similar effect of increased glass surface on the rate of reaction of nitric oxide and chlorine

has been noted by Kiss[9] and by Trautz and Henglein.[10] A duplicate experiment fully confirms Expt. 4, the constants being accelerated in an analogous manner.



The experiments at the lower temperature, 0°, show a different state of affairs. Acceleration in the constants in Expt. 6 is very slight; while with

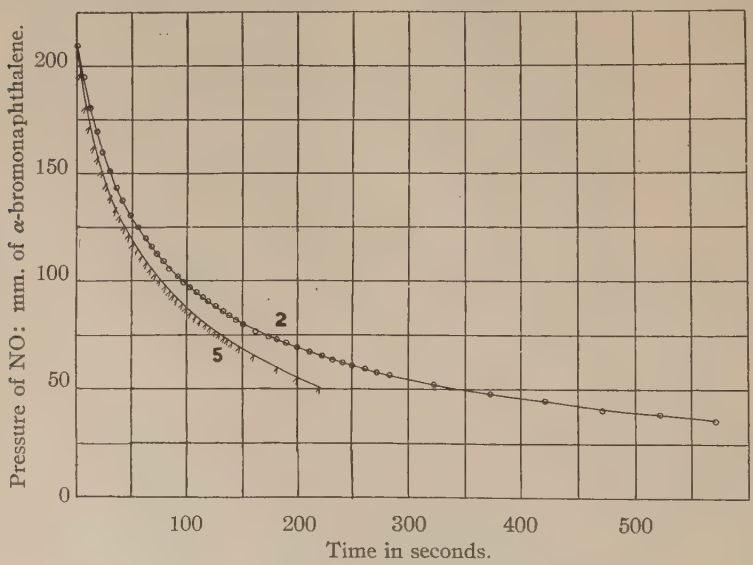


Fig. 3.—Temperature, 30°. No. 5, large surface. No. 2, small surface.

the small surface in Expt. 9 the constants have increased four-fold at the end of the run. This large increase in the case of the small surface may be

[9] Kiss, *Rec. trav. chim.*, **4**, 112 (1923).

[10] Trautz and Henglein, *Z. anorg. Chem.*, **110**, 246 (1920).

due to the formation of nitrogen trioxide as a side reaction. The state of dryness in the two reaction vessels is not the same, considering the increase in surface-to-volume ratio of approximately 140 times produced by the glass wool, and it is not possible to pump off traces of moisture at the low temperature. The experiments of Baker[11] indicate that the decomposition of nitrogen trioxide is catalyzed by moisture. Another influence that should be considered and which would operate in the same direction is the imperfect state of the gas, nitrogen tetra-oxide, so close to its boiling point. It will be noted that the pressures used in Expt. 9 were considerably higher

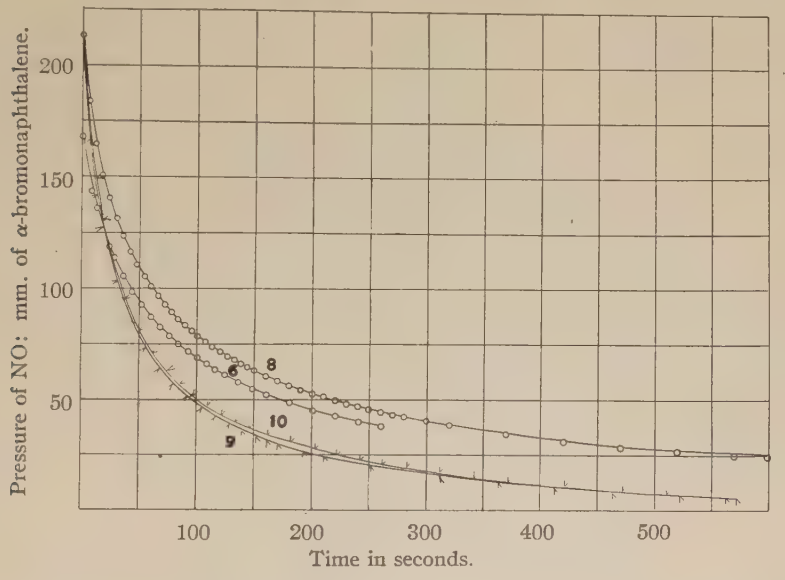


Fig. 4.—Temperature, 0°. Nos. 6 and 8, large surfaces. Nos. 9 and 10, small surfaces.

than those in Expt. 6. Other experiments, not included in the tables, closely agree with Expts. 6 and 9. In all cases, however, where acceleration in the velocity constants occurs, it is noticeable only in the latter half of the reaction.

Plots of some of the experiments are shown in Figs. 3 and 4. It was from these curves that the slopes were read. The curves give some idea of the accuracy of the data and check the calculated initial pressures. No evidence of autocatalysis was apparent from the curves.

A comparison of the velocity measurements in the present work with those of Bodenstein shows a fairly good agreement. The average of all the experiments at 30° with the small surface is 5.43×10^{-7}. In the first half of all the experiments at 0° there is little difference between the large

[11] Baker, *J. Chem. Soc.*, **91**, 1862 (1907).

and small surface. Taking an average of all the experiments when 50% of the nitric oxide has been converted gives a value of 9.10×10^{-7} for the lower temperature. These constants may be converted into terms of moles per liter with time expressed in minutes by the formula

$$K_c = 2 \times 60 K_p \frac{1}{a^2} = 2 \times 60 K_p \left(\frac{1.5}{13.6} \times \frac{1}{760} \times \frac{273}{T} \times \frac{1}{22.4} \right)^{-2}$$

(It is necessary to multiply by two, since Bodenstein used only one-half the measured pressure of nitric oxide in the calculation of his velocity constants.)

The table shows the comparison.

	273°K.	303°K.	$\frac{K_{t+10}}{K_t}$
k_c(Bodenstein)	2.09×10^{-6}	1.70×10^{-6}	0.933
k_c(Our value)	2.60×10^{-6}	1.94×10^{-6}	.916

The customary 10° temperature coefficient is given in the last column.

Negative Temperature Coefficient

The negative temperature coefficient of this reaction seems to point to an unstable intermediate compound which is in the state of rapid equilibrium. Gay Lussac, in 1842, first stated the general principle that in complex reactions, that compound is first formed which is the least stable. Skrabal[12] presents the corollary that, when intermediates are possible, a slow reaction produces the most stable end product. Of the possible intermediates, N_2O_2 and an iso N_2O_4 may be considered. The latter would probably be a peroxide as suggested by G. N. Lewis.[13] The reactions involving these intermediates would be represented as follows

$$2NO \rightleftharpoons N_2O_2 \text{ (fast)} \quad (1)$$
$$N_2O_2 + O_2 = 2NO_2 \text{ (measurably slow)} \quad (1a)$$
$$2NO + O_2 \rightleftharpoons N_2O_4 \text{ (iso) (fast)} \quad (2)$$
$$\text{(iso)}N_2O_4 = 2NO_2 \text{ (measurably slow)} \quad (2a)$$

Assuming that Reactions 1 and 2 are in rapid equilibrium, the reaction the speed of which we were measuring would be that of 1a or 2a. In all cases the establishment of the equilibrium between nitrogen dioxide and the tetra-oxide is immediate as far as we are concerned. Since an increase in temperature would shift the equilibrium in Reactions 1 and 2 toward the left, we should expect a negative temperature coefficient. Whenever, then, an equilibrium of the type given above is superimposed upon a normal reaction, a reversed temperature coefficient should result. Skrabal[14] has described such a reaction in solution, between iodic acid and sulfurous acid. As to what intermediate is formed in the reaction between nitric oxide and oxygen, that question awaits more experimental evidence for its answer. A minute amount of the intermediate would account for the speed of the

[12] Skrabal, *Z. Elektrochem.*, **14**, 529 (1908).
[13] Lewis, *Chem. Reviews*, **1**, 231 (1924).
[14] Skrabal, *Z. Elektrochem.*, **21**, 461 (1915).

reaction. An attempt is being made to isolate and identify an intermediate at liquid-air temperatures.

Summary

1. The velocity of the reaction between nitric oxide and oxygen has been studied at 0° and 30°. The reaction was found to be one of the third order at the higher temperature; while the acceleration in the velocity constants at 0° may be due to the formation of N_2O_3 or to the imperfect state of N_2O_4.

2. A large increase in surface-to-volume ratio by the introduction of glass wool into the reaction chamber caused a marked acceleration in the velocity constants in the latter half of the reaction at 30°; the acceleration was less marked at the lower temperature.

3. No evidence of autocatalysis was obtained.

4. The negative temperature coefficient of the reaction has been ascribed to intermediate compound formation.

BIOGRAPHY

Rudolph Leonard Hasche was born June 20, 1896 at Doon, Iowa. He entered Tarkio College in 1914 and received the B.S. degree from that college in 1918. He served three months during the war with the Chemical Warfare Service, American University, Washington, D. C. He entered Washington and Jefferson College in the late fall of 1918 and received the M.S. degree from that institution in 1919. During the years 1919–23, he was Instructor in Chemistry at Carnegie Institute of Technology. He spent one summer in graduate work at the University of Chicago and took part-time graduate work at the University of Pittsburgh during the years 1921–23. He was employed as chemist by the Pittsburgh Testing Laboratories the summers of 1922 and 1923. He entered the Johns Hopkins University in the fall of 1923 where he has been engaged in graduate work to the present time.